

AMENDED SPECIFICATION

Reprinted as amended in accordance with the Decision of the Superintending Examiner, acting for the Comptroller General dated the twenty third day of June 1970, under Section 14, of the Patents Act, 1949.

PATENT SPECIFICATION

NO DRAWINGS

L108.327

L108.327



Date of Application (No. 31956/65) and filing Complete Specification: 27 July, 1965.

Application made in United States of America (No. 387,787) on 5 August, 1964.

Complete Specification Published: 3 April, 1968.

Index at acceptance:—C2 C(3A13B2A1, 3A13B2E, 3A13B2F3).

Int. Cl.:—C 07 c 39/00.

COMPLETE SPECIFICATION

Process for Purifying Phenols

We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

This invention relates to the purification of a phenol produced by the acid-catalyzed cleavage of the hydroperoxide resulting from the oxidation of a secondary alkyl aromatic hydrocarbon, and particularly to the purification of phenol produced by acid cleavage of the hydroperoxide resulting from the oxidation of cumene.

Phenol is prepared by the partial oxidation of cumene to cumene hydro-peroxide followed by acid catalyzed cleavage of the hydroperoxide to form a cleavage reaction mixture containing phenol, acetone and unreacted cumene. The cleavage reaction mixture is neutralized and thereafter fractionated to separate the phenol product from the higher and lower boiling constituents of the cleavage reaction mixture. Even with an efficient fractionation column the phenol fraction contains small but detrimental amounts of impurities formed during the oxidation, cleavage, and phenol separation sequence. The impurities remaining in the phenol fraction comprise carbonyl compounds including diacetone alcohol, hydroxy acetone, acetone trimers and principally the acetone condensation product mesityl oxide which is practically inseparable from the phenol by simple

distillation methods. The carbonyl compounds are detrimental in even small amounts because they have color-forming tendencies which render the phenol product unacceptable for many commercial applications.

It is an object of this invention to substantially eliminate the impurities comprising carbonyl compounds from a phenol fraction recovered from a reaction mixture resulting from the acid cleavage of the hydroperoxide resulting from the oxidation of a secondary alkyl aromatic hydrocarbon, particularly cumene.

The production of phenol by the partial oxidation of cumene to cumene hydroperoxide and subsequent acid cleavage of the hydroperoxide to phenol and acetone is well known to the art. The process has been applied to the production of phenols in general wherein a secondary alkyl aromatic hydrocarbon corresponding to the desired phenol is oxidized to the hydroperoxide which is subsequently cleaved to form the desired phenol and an aliphatic ketone. While the present description is principally with reference to the purification of the phenol fraction recovered from a reaction mixture resulting from the acid cleavage of the hydro-peroxide resulting from the oxidation of cumene, the process may also be utilized to eliminate impurities comprising carbonyl compounds from a phenol fraction recovered from a reaction mixture resulting from the acid cleavage of the hydroperoxide oxidation product of a secondary alkyl aromatic hydrocarbon, for example, *o* - isopropyltoluene, *m* - isopropyltoluene, *p* - isopropyltoluene, *p* - diisopropylbenzene, *sec* - butylbenzene and β - isopropyl-naphthalene.

5 The present invention relates to a process for the purification of a phenol which has been prepared by the steps of partial oxidation of a secondary alkyl aromatic hydrocarbon to form an alpha hydroperoxy derivative thereof, acid - catalyzed cleavage of said derivative to form a phenol and an aliphatic ketone, neutralization of the cleavage reaction mixture, and separation from the neutralized reaction mixture of a fraction containing the phenol and impurities comprising carbonyl compounds, characterized in that at least a portion of said impurities comprising carbonyl compounds are separated from the phenol fraction by admixing H₂O with the fraction, contacting the resultant mixture at a temperature in the range of from 150 to 250° C with particles of a catalytic composition consisting of silica - alumina, silica - zirconia or silica-alumina - zirconia containing from 70 to 90% by weight of silica thereby converting said carbonyl compounds to compounds having lower boiling points, and distilling said compounds from the phenol.

25 Other objects and embodiments of this invention will become apparent in the following detailed specification.

30 In accordance with the present process, water or steam is admixed with the phenol fraction recovered from the cleavage reaction mixture and the water-phenol mixture is contacted with the catalytic composition at a temperature of from 150 to 250° C. The water-phenol mixture should comprise at least from 0.1 to 20 wt.% water, or steam corresponding to an equivalent amount of water. The phenol is preferably treated in the liquid phase although some vapor phase phenol is usually present. The optimum contact time is, of course, determined in part by the particular temperature employed and in part by the catalytic composition employed. A contact time equivalent to a liquid hourly space velocity of from 0.1 to 5.0, and preferably from 0.2 to 2.0, is suitable. A pressure in the range of from atmospheric to 17 atmospheres is usually employed although the exact pressure is not critical.

50 The catalytic compositions useful in effecting the process of this invention particularly include silica-alumina compositions. The silica-alumina compositions include the aluminum silicate clays of the bentonite type which have been activated by acid treatment. However, the synthetically prepared silica-alumina compositions comprising by weight from 70% to 90%, silica are preferred catalytic compositions. These compositions are readily prepared by methods known to the art. One such method comprises coprecipitation or cogellation of silica and alumina from a common solution. For example, aqueous solutions of sodium silicate (common water glass) and aluminum sulfate are mixed together and sufficient acid, such as hydrochloric or sulfuric acid, is added

thereto to form a precipitate or gel. Another method comprises impregnating a silica gel with a suitable aluminum compound which is subsequently convertible to alumina. For example, aluminum hydroxide is precipitated from an aqueous solution of a suitable aluminum salt, such as aluminum sulfate, in the presence of silica gel immersed in the solution. The resulting composite is thereafter heated at elevated temperature and the impregnated hydroxide converted to alumina by thermal decomposition. Alternatively, the silica gel can be impregnated with a decomposable aluminum salt which will form alumina on subsequent heating. Aluminum nitrate is suitable for this purpose and can be impregnated on the silica gel by immersing the gel in an aqueous solution of aluminum nitrate.

85 The composition of silica and alumina prepared by methods such as are set out above, is generally water-washed to remove soluble salts therefrom and thereafter dried, usually at a temperature of from 95° C to 200° C. The composition is thereafter subjected to calcination at a temperature of at least 475° C, and generally at a temperature of at least 475° C to 800° C. A particularly preferred temperature is in the range of from 600° C to 700° C. Calcination can be effected in any suitable atmosphere. Usually calcination is effected in the presence of air or other oxidizing media although calcination may also be effected in a reducing atmosphere such as hydrogen, or an inert atmosphere such as nitrogen.

100 Although silica-alumina is a preferred catalytic composition, certain other compositions namely, silica - zirconia, and silica - alumina-zirconia containing from 70 to 90% by weight of silica exhibit desirable catalytic characteristics and may be utilized.

105 The treatment of the phenol fraction with water in contact with, for example, the silica-alumina catalyst, and separation of the carbonyl compound conversion products from the phenol, may be carried out in two separate steps or in one and the same step. By the process herein described, the impurities comprising carbonyl compounds are converted to lower boiling conversion products readily distillable from the phenol, or separable therefrom by means of a stripping gas such as nitrogen, or by a combination of both stripping and distillation. Other impurities which may be present are incidentally separated pursuant to the present process. For example, in the separation of excess water from the phenol by distillation methods, methyl-benzofuran, generally present in at least trace amounts, is recovered as a portion of the steam distillate. Purification of crude phenol by condensation of the impurities contained therein with the requisite amount of the phenol product has previously been proposed. Thus, in U.K. Patent Specification No. 865,677 there is des-

cribed and claimed the process for the purification of phenol derived from cumene and containing colour-forming impurities including aliphatic α - hydroxy carbonyl compounds, which process comprises subjecting the impure phenol at an elevated temperature to conditions which will cause the substantially complete condensation of the aliphatic α - hydroxy carbonyl compounds with phenol to form benzofurans, and separating the phenol substantially completely from the benzofurans. By the process of the present invention the carbonyl impurities are hydrolysed by the water added to the mixture prior to contact with the catalyst.

The following examples are presented to illustrate the process of this invention.

EXAMPLES I & II

Phenol, fractionally distilled from a neutralized cumene hydroperoxide cleavage reaction mixture, was analyzed by gas-liquid chromatography and found to contain mesityl oxide. The phenol, commingled with steam, was charged to a vertical tubular reactor containing 200 cubic centimeters, or 120 grams, of 3.2 mm silica-alumina pellets comprising 88% by weight silica and 12% alumina disposed in a fixed bed therein. The reactor was maintained at about atmospheric pressure and at a temperature of 190° C., and the phenol and steam rates were adjusted to give streams containing variable amounts of water. The reactor effluent was continuously withdrawn from the reactor and cooled. Analysis of feed and products, shown below, indicate substantial conversion of mesityl oxide to acetone, which can be readily removed by distillation.

EXAMPLE

	I	II
Charge rate, cc/hr.	40	100
Water, wt. %	2.0	5.0
Feed Analysis, wt. %		
Acetone	.0010	.0010
Mesityl oxide	.1940	.1940
Product Analysis, wt. %		
Acetone	.1467	.1193
Mesityl oxide	.0060	.0041

EXAMPLE III & IV

A phenol fraction recovered by distillation of a neutralized cumene hydroperoxide cleavage reaction mixture and containing carbonyl impurities, principally mesityl oxide but also diacetone alcohol, hydroxy acetone and acetone trimer, was treated to convert complex carbonyl compounds to acetone. The phenol fraction was combined with about 10 wt. % water. The phenol was then charged through a steam heated line to a vertical tubular reactor at a liquid hourly space velocity of 0.5, the reactor containing 100 cubic centimeters of silica-alumina pellets comprising 76% by weight silica and 24% alumina in a fixed bed.

The reactor was maintained at about 5 atmospheres and at a temperature of 205° C. Charge and product analyses, shown below, again show substantial conversion of mesityl oxide to acetone, and also show formation of other miscellaneous compounds more volatile than phenol, which again are removable by distillation.

EXAMPLE

	III	IV
Feed Analysis, wt. %		
Acetone	.0036	.0036
Mesityl oxide	.1489	.1489
Miscellaneous	.0915	.0915
Product Analysis, wt. %		
Acetone	.1788	.1606
Mesityl oxide	.0063	.0067
Miscellaneous	.1349	.1868

EXAMPLE V

A phenol fraction recovered by distillation of a neutralized cumene hydroperoxide cleavage reaction mixture and containing acetone polymers was converted to a phenol product containing separable impurities utilizing a silica - zirconia composition comprising by weight about 90% silica as the catalyst. 200 cubic centimeters of catalyst in the form of 3.2 mm spheres was disposed in a fixed bed of a vertical tubular reactor. The phenol was charged to the reactor together with steam so as to form a water-phenol charge containing about 5 wt. % water. The water-phenol was charged at a liquid hourly space velocity of approximately 1, the reactor being maintained at a temperature of about 190° C at a pressure of about 3.4 atmospheres. The reactor effluent was recovered and analyzed, as shown below.

Feed Analysis, wt. %

Acetone	.01
Mesityl oxide	.16
Miscellaneous	.14

Product Analysis, wt. %

Acetone	.18
Mesityl oxide	.01
Miscellaneous	.03

A less precise method of analysis was used in this example. Again, however, conversion of mesityl oxide to acetone is nearly complete.

WHAT WE CLAIM IS:—

1. A process for the purification of a phenol which has been prepared by the steps of partial oxidation of a secondary alkyl aromatic hydrocarbon to form an alpha hydroperoxy derivative thereof, acid-catalyzed cleavage of said derivative to form a phenol and an aliphatic ketone, neutralization of the cleavage reaction mixture, and separation from the neutralized reaction mixture of a fraction containing the phenol and impurities comprising

carbonyl compounds, characterized in that at least a portion of said impurities comprising carbonyl compounds is separated from the phenol fraction by admixing H_2O with the fraction, contacting the resultant mixture at a temperature of from 150 to 250° C with particles of a catalytic composition consisting of silica - alumina, silica - zirconia, or silica-alumina - zirconia, containing from 70 to 90% by weight of silica thereby converting said carbonyl compounds to compounds having lower boiling points, and distilling said compounds from the phenol.

2. Process as claimed in claim 1, characterized in that the phenol fraction admixed with H_2O is contacted with particles of a catalytic composition consisting of silica and alumina which contains from 70 to 90% by weight of silica.

3. Process as claimed in one of the claims 1 and 2, characterized in that the phenol fraction to be purified has been recovered from the

reaction mixture resulting from the acid cleavage of the hydroperoxide produced by the oxidation of cumene.

4. Process as claimed in one of the claims 1 to 3, characterized in that the phenol fraction to be purified is admixed with from 0.1 to 20 wt.% H_2O .

5. Process as claimed in one of the claims 1 to 4, characterized in that the mixture of H_2O and the phenol fraction to be purified is passed into contact with the catalytic composition at a liquid hourly space velocity of from 0.1 to 5.0.

6. Process for the purification of a phenol prepared from a secondary alkyl aromatic hydrocarbon, substantially as described.

J. Y. & G. W. JOHNSON,
Furnival House,
14-18, High Holborn,
London, W.C.1.
Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1970.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.